

THE HIGH VACUUM DISTILLATION
OF THE METHYL ESTERS
OF THE FATTY ACIDS FROM KAFIR FAT

by

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INTRODUCTION

Fats is the general name of the class of organic compounds consisting of the glyceryl esters of fatty acids. As found in nature, these are always mixtures, that is, esters of glycerine with different fatty acids in various proportions. The analysis of the fat therefore entails the separation and identification of the fatty acids of which it is composed. Since the properties and, therefore, uses of a fat depend upon its composition, this information would lend greatly to the development of further uses of a particular fat. For this reason, it was thought well worth while to conduct a study on the composition of kafir fat.

In analyzing a fat two procedures are optional. One may run a series of analytical constants such as iodine no., saponification value, acetyl value, etc., which give the amount of unsaturation, mean molecular weight, etc. These are all average values, and give an accurate picture of the character of the fat as a whole, and are sufficient usually to determine the type of fat, its source, its purity and its possible uses. The other procedure is to convert the fat into some other type of compound which can be separated into the various constituents, and then examine and identify these portions separately. The latter

method is the one undertaken in this study.

Since neither the fat nor the fatty acids of which it is composed are easily separable by distillation (7), the fatty acids were converted into methyl esters, which could be fractionally distilled under vacuum in a suitable apparatus. In addition to the lower boiling points of these esters as compared to those of the fatty acids, association of the molecules, which occurs with fatty acids (19), is prevented by "protection" of the carboxyl group by esterification. This type of work was first carried out on coconut oil by Haller and Youssoufian in 1906 (11), and applied later to the analysis of many oils and fats such as olive oil (14), castor oil (12), linseed oil (13), pinenut oil (1), Brazil nut oil (24), sunflower seed oil (16), cantaloup seed oil (3), and corn oil (4). Since the esters are high-boiling at ordinary pressures, the use of vacuum is necessary to prevent excessive temperatures and was used by Elsdon (8) and by Stokoe (26) in distilling the esters of coconut oil. Early attempts consisted of distillations from flasks without the use of columns. Later workers (6, 19, 20, 27) have used fractionating columns to great advantage, eliminating much of the numerous re-fractionations formerly required and also preventing

excessive heating and handling.

The problem then resolves itself into three major phases: (a) working out a suitable method for the quantitative conversion of the fat into the methyl esters, so that the esters are representative of the composition of the original fat; (b) construction of an apparatus capable of fractionally distilling these esters; and (c) the actual fractionation of these esters and the identification of the fractions by physical and chemical means.

EXPERIMENTAL METHODS

Preparation of the Esters

Two methods can be used to prepare the esters. Haller (11) prepared them by alcoholysis, which consisted of boiling the fat with a large excess of methyl alcohol (about 2:1 by wt.) for twenty or more hours. This procedure makes use of the mass law for the equilibrium set up, and depends also on the relative reactivity of the methyl alcohol and the glycerine.

Armstrong, Allen and Moore (2), on the other hand, prepared the esters by first forming the acids, separating the saturated from the unsaturated acids, and then esterifying the two portions separately, using sulfuric acid.

All present methods are modifications of one or the other of these two methods. While the former has the advantage of simplicity and economy, the latter method is more quantitative, and especially desirable if the unsaponifiable material runs high. It allows for separation of the unsaturated from the saturated esters. This last separation is important because the saturated and unsaturated esters of two acids containing the same number of carbon atoms cannot be separated by distillation (18). It also simplifies calculation of the composition of the fractions obtained by distillation. In this investigation, it did not seem necessary to do this, because iodine numbers on the fat indicated it to be composed mostly of unsaturated acids.

Prior to the adoption of the described method of esterification, it was considered necessary to investigate the several procedures which have been proposed. On one sample in which methyl alcohol was used directly, there was evidence of incomplete esterification. On a second sample in which dry HCl gas was passed into the methyl alcohol before adding the fat, a darkened product resulted. A similar trial was conducted on a sample in which the usual steps of saponification and conversion to the acids were followed. A yield of nearly 100 per cent was obtained and the resulting acids were obtained in a very pure condition.

The latter method was chosen because the glycerine was removed by complete saponification. The presence of glycerine gives erroneous iodine values due to the formation of acrolein.

Two separate quantities of fat, extracted from Black-hull kafir grain with Skelly Solve B, were saponified. A weighed amount of fat, 634.8 g., was refluxed with 1905 cc. of methyl alcohol and 419 cc. of 40 per cent NaOH for an hour and a half. The alcohol was distilled off and the soap dissolved in water and acidified with HCl. The acids were allowed to clear, separated, washed thoroughly with hot water, and dried for an hour at 110° C. Similarly a second sample of 666.6 g. of fat was saponified with 433 cc. of 40 per cent NaOH and 1970 cc. of alcohol.

The quantity of fatty acids was divided into two portions and esterifications were carried out in 5-liter flasks. In the first run, 562.2 g. of fatty acid were refluxed for five hours with 1700 cc. of methyl alcohol, with a steady stream of dry HCl gas bubbling through the solution. The mixture turned rather dark. Half the alcohol was distilled off, water added and the ester layer extracted with Skelly Solve, washed with dilute sodium carbonate, then water, and recovered. It was necessary to use vacuum and bubble nitrogen gas through the mixture to remove all the solvent. The yield was 556.5 grams. Similarly, 506.9g.

of fatty acid in the second run yielded 518.5 g. of esters. The iodine values for the crude esters were 106.6 and 105.9, which corresponded closely with that of the original fat. Likewise the saponification values of the esters were 169.1, 168.0, and 169.7, with an average of 168.9 which also corresponded with the fat. The crude esters were light brown in color and had a semi-liquid, semi-crystalline form.

The Apparatus

The apparatus was constructed entirely of glass, all joints being ground glass and all valve manipulations controlled by stopcocks. The still retort was constructed from a two-liter distilling flask and was attached to the column with a large 35 mm. ground joint.

The column was made from a five foot length of 25 mm. pyrex tubing, filled to a height of 53 inches with single turn glass helices. This type of packing was selected because of its high efficiency as investigated by Fenske, Quiggle and Tongberg (9). The helices were made from 4 mm. soft glass rod by heating in an oxygen-gas flame and winding onto a motor-driven steel shaft (22, 25, 28, 29). This yielded a long glass helix which was then broken into individual turns having the dimensions of diameter of turn 4 mm., and diameter of fibre 0.5 mm. Data obtained

by distilling a carbon tetrachloride-benzene mixture (15, 23) gave efficiencies of 13 to 17 theoretical plates, giving an average value of the H. E. T. P. (height of equivalent tower plate) of 3.6 cm. or 1.4 inches. The column was connected to an evacuating system consisting of cold traps and an oil diffusion pump backed by a mechanical pump. The pressure in the flask, when evacuated, was 4.0×10^{-3} mm. Hg as determined by a McLeod gauge.

Due to the high-boiling nature of the esters, the column had to be well insulated. It was first covered with two layers of sheet asbestos, then wound with 30 feet of No. 29 chromel resistance wire by which the column could be heated if necessary, and then covered with another layer of sheet asbestos. The turns of wire were spaced about one half an inch apart. The heating of the column was controlled through an external resistance by which the wattage could be varied from 50 to 300. The entire column was wrapped with rock wool to a thickness of one inch. The temperature of the asbestos insulation, as evidenced by thermocouples embedded in the asbestos, was controlled to a temperature slightly lower than that of the vapors at the top of the column. A straight piece of glass tubing as an air condenser was found to be sufficient to condense the esters, although a water condenser was also used. The air condenser and the

arm leading to the receiver were wound with No. 24 nichrome wire so that any esters which might solidify there could be melted and run down into the receiver. The still retort was heated directly by an electric heater of 1000 watts, which was controlled by means of a tubular rheostat.

A system of stopcocks was improvised so that receivers could be exchanged and exhausted without breaking into the vacuum of the column. The entire system was tested for leaks with an electric discharge produced by a spark coil.

The general arrangement of the apparatus is shown in Plate I.

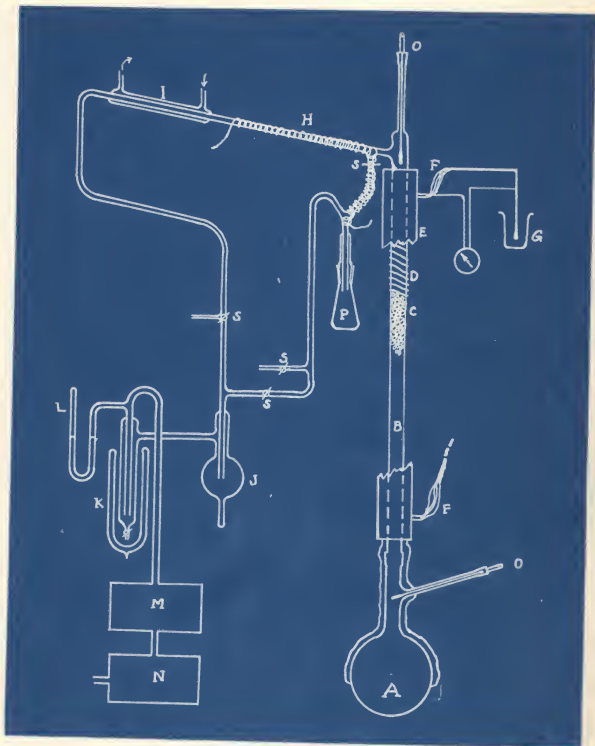
Distillation of the Esters

The crude esters, amounting to 944.5 g., flask and a few small boiling chip and glass wool were added to prevent bumping (21). Due to superheating and the development of a leaky stopcock, the first distillation was unsatisfactory. The solid material in the flask, after the distillation, was extracted with Skelly Solve and the solid esters obtained from it retained along with one sharp low-boiling fraction; the rest of the esters were returned to the flask to be redistilled. The second distillation proceeded more uniformly, although considerable difficulty was experienced in maintaining uniformity of

EXPLANATION OF PLATE I

A	Still retort
B	Fractionating column
C	Glass helices packing
D	Asbestos insulation and heating wire
E	Rock wool insulation
F	Thermocouples
G	Cold junction of thermocouples
H	Air condenser and heating wire
I	Water condenser
J	Expansion trap
K	Cold trap
L	Mercury manometer
M	Oil diffusion pump
N	Cenco Hi-vac motor-driven pump
O	Thermometers
P	Receiver flask
S	Stopcocks

Plate I



temperature at the high vacuum at which the column was operating.

The first and the last fractions were slightly colored while the majority of the esters were clear and colorless, with no appreciable odor. At no time was the distillate taken off at rates faster than one drop per second. The time for the distillation was 10 hours. It was found necessary to heat the column continually. Twelve fractions were taken, which, with the fractions from the first run, totaled 794.0 g., corresponding to a loss of 150.5 g. The residue in the flask was charred, showing excessive decomposition, probably accounting for the large loss of material.

The data for the distillation are recorded in Table 1.

Analysis of the Fractions

Standard methods were used to determine the iodine number (Wijs) (17), saponification values (17), and refractive indices on the fractions obtained by distillation. These data are recorded in Table 1.

The relationships existing between the various properties and quantities of fractions distilled are represented graphically in Figs. 1, 2, and 3.

Table 1. Analysis of the fractions

Frac.:	Wgt.:	Boiling	Melting	Refract.:	Iodine	Sapon.
:	g.:	Range	Point	Index	No.:	No.:
:	:	°C	°C	25°C	:	:
1	1.6	below 100	-----	1.4578	---	296.7
2	1.7	125-135	17.3-18.7	1.4674	---	297.5
2a†	31.0	153-156	27.7-28.5	1.4435	12.0	215.1
3	65.9	133-143	28.4-29.1	1.4420	14.2	309.2
4	19.1	149-156	28.9-29.4	1.4624	94.9	304.7
5	37.3	153-156	28.2-28.9	1.4649	114.2	197.0
6	86.1	156-156	11q.	1.4667	130.5	192.8
7	88.3	159-160	11q.	1.4667	139.6	192.7
8	91.2	159-160	11q.	1.4669	139.3	193.5
9	45.4	160-162	11q.	1.4669	139.6	194.6
10	87.2	162-163	11q.	1.4669	139.4	193.0
11	95.5	163-164	11q.	1.4669	137.5	192.0
12	36.9	164-170	11q.	1.4671	137.5	192.0
13†	13.2	100-200	---	----	147.4	116.4
14†	33.0	200-300	---	----	116.8	100.1
15‡	62.6	300-340	---	----	66.1	42.9

*Recrystallized from methyl alcohol at 0° C.

**Each value of Iodine No., and Sapon. No. is an average of triplicates and duplicates respectively.

†Fraction obtained from first distillation. High temperature due to leak in apparatus.

‡Fractions 13, 14, and 15 were distilled from a 200 cc. distilling flask under vacuum, composed of residues extracted from flask, and solid esters from first dist'n.

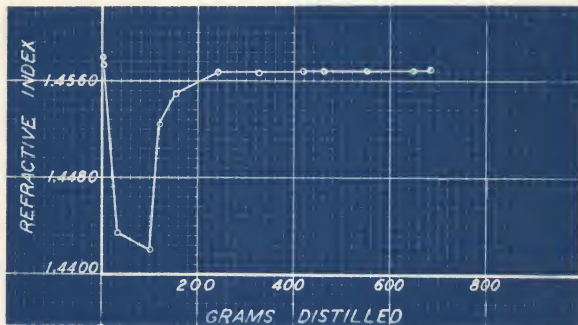


Fig. 1. Trend of the refractive index.

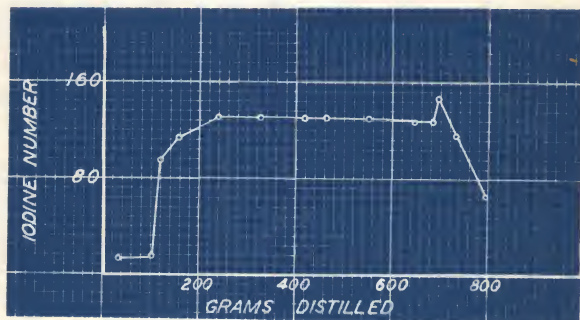


Fig. 2. Trend of the iodine number.

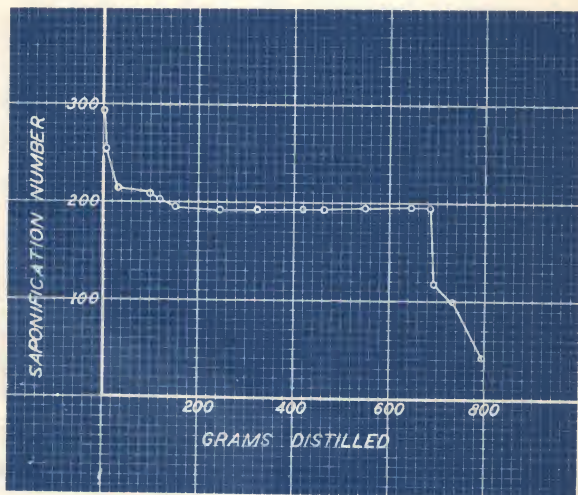


Fig. 3. Trend of the saponification number.

DISCUSSION

The pressure in the system, when operating without presence of material, was adequately and rapidly reduced to values of 4×10^{-3} mm. by the mechanical and oil diffusion pumps. For the distillation pursued, a salt-ice-water cold trap was sufficiently adequate to catch any of the products of decomposition. At this low pressure, leaks were readily detected with a high voltage discharge. The presence of the slightest leak was found to cause great fluctuations in the boiling point. The temperatures of the vapors were a little higher than the accepted values at low pressures. This was probably due to a slight superheating necessary to force the vapors through the length of the column. The temperatures of the vapor entering the column were generally about 50° higher than that of the vapor at the top of the column. In the second distillation, the highest temperature attained by the vapors entering the column was 220° C.

The actual distillation had to be accomplished slowly since a condition of too rapid boiling resulted in flooding of the column and a rise in temperature. The best results were obtained when the condensed vapors were not permitted to block the vapor passage in the condenser. It was found inadvisable to attempt to distill over solid materials since

excessive heatings were required. At high temperatures, decomposition, accompanied by smoking and carbonization, occurred in the flask.

An inspection of Table 1 reveals the fact that of the fractions below 5, all crystallized from alcohol; in fact, they all solidified in an ice bath without alcohol. By recrystallizing from methyl alcohol several times at 0° C., methyl palmitate was identified in fractions 2a, 3, 4 and 5, by the range of melting points 28.2°-29.4° C. The saponification values for these fractions agree tolerably well with this conclusion, although the value for fraction 2a indicates a still lower acid present. Fraction 2 had a saponification value between that of the myristate and laurate esters, but the melting point was 17.3°-19.7° C. Fraction 1 obviously contained an ester of less than 13 carbon atoms since methyl laurate has a saponification number of 262 while this fraction had a value of 296.7. Not enough was obtained, however, to identify it. Contrary to previous investigations (10), no methyl stearate was found in any of the fractions.

An observed correlation is noted between the refractive index and the iodine value, which is to be expected, since the refractive index increases with the number of double bonds. The fractions with high iodine values

were tested for the presence of saturated esters by dissolving the respective fractions in methyl alcohol and crystallizing out the saturated esters at 0° C. Fraction 10 had only traces of saturated esters, fraction 11 had slightly more, and fraction 12 crystallized out a perceptible amount. Fractions 6, 7, 8, and 9 gave no crystallizations from alcohol. Moreover, the amount of saturated esters in fraction 12 was small enough to neglect.

The fractions 13, 14, and 15, which were distilled from a small distilling flask under vacuum from a water aspirator, showed definite signs of decomposition as evidenced by smoking and charring. The sharp peak in the iodine number curve is probably due to the formation of some unsaturated decomposition products (6). The sudden drop in the saponification value is difficult to explain. From a consideration of the foregoing sentences, it is quite probable that these fractions are not resolvable.

The calculation of per cent composition of the low iodine value fractions was made with the assumption that the proportion of oleic to linoleic was the same as in fraction 6. Thus, calculating from the saponification number, the amounts of methyl myristate and palmitate are calculated for fractions 2a and 3. In fractions 4 and 5, however, the saponification number indicated the absence

of methyl myristate and the composition was calculated as palmitic, oleic and linoleic esters. Fractions 6-12 have constant properties and these agree well with methyl oleate and linoleate. By brominating the fatty acids prepared from these fractions, linolenic acid was proved to be absent, since no hexabromide could be obtained. The tetrabromide of linoleic was formed, however, and identified by its melting point of 115° - 116° C. Therefore, the compositions of fractions 6-12 were calculated on the basis of iodine values. The calculation of fractions 13, 14 and 15 was not attempted since the saturated component could not be identified.

The foregoing calculations are summarized in Table 2, giving the calculated composition of each fraction and the total amount of each component present. At the bottom of the table two different sets of percentages are given. One set is calculated on the basis of the amount of esters distilled, assuming the lost material to be of average composition. The other set of percentages is given on the basis of the total material placed in the flask and represents the minimum amount of each component present. The true value probably lies somewhere between the two. The oleic and linoleic percentages will be necessarily low because they do not include that which is undoubtedly present in fractions 13, 14, and 15.

Table 2. Calculated composition of fractions

Fract. :	Myristic :	Palmitic :	Oleic :	Linoleic :	Unresolved Vol. Residues
1*					
2	1.7				
2a	11.5	16.5	1.5	1.6	
3	11.1	47.4	3.6	3.8	
4		5.2	6.8	7.1	
5		4.5	16.0	16.8	
6			41.4	43.7	
7			42.5	42.8	
8			45.6	45.6	
9			22.5	22.9	
10			44.5	42.7	
11			49.8	45.7	
12			19.2	17.7	
13-15					110.9
Grams	24.3	73.6	293.4	290.4	110.9
% dist'd.	3.06	9.28	37.00	36.60	13.98
% original	2.57	7.80	31.05	30.80	13.15

* Composed of low molecular weight ester of less than 12 carbon atoms amounting to less than 0.2%.

SUMMARY

1. The methyl esters of the fatty acids from kafir grain have been prepared. These have been subjected to a high vacuum distillation in an efficient all-glass fractionating column.

2. The fractions have been analyzed and the constitution of the kafir fat has been determined.

3. The kafir fat has been shown to consist essentially of oleic and linoleic acids, with palmitic and myristic acids present in smaller amounts. Evidence has been found of a constituent having a molecular weight lower than that of lauric acid.

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